LIQUID-LIQUID EXTRACTION WITH SOLUTE RETURN

BY

GEORGE FRANCIS ASSELIN

B.S., University of Illinois, 1943
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
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This investigation was concerned with the effect of returning reflux in solvent extraction processes involving four or five components. Two of these were the essentially immiscible solvents, water and n-amyl alcohol, and two of the others were the compounds to be separated. When a fifth was used, it served to modify the equilibrium distribution relationships. The effects of the relative amounts of the two solvents, the total concentration of the two compounds in the feed, and the composition of the feed on a solvent-free basis were also observed.

Equipment

A five-stage extraction system was used in preference to a packed column because it provided a more definite number of equilibrium contacts and permitted sampling at definite, intermediate stages. The latter is important when the equipment is used to follow the course of extraction in a system for which complete equilibrium data are not available.

Each stage consisted of a pump, a short, packed column, and a settling chamber similar in design and construction to that used by Knox *et al.* (4). The reflux section was composed of a reflux splitter, a small spray type extraction column, and an evaporator similar to Kemmerer's design (3). Reflux was provided in such a manner that the composition of solutes on a dry basis was the same in the aqueous stream, leaving, and in the solvent, entering, at one end of the extractor. The feed was introduced at the other end of the system, so that only the part of a complete extraction unit on one side of the feed was used. Thus only one purified product could be obtained, namely, the less readily extracted solute.

Equilibrium Data

The system, oxalic acid - succinic acid - water - n-amyl alcohol, was selected for the major part of the experiments.

This system was chosen because it was convenient to analyze and because its components were relatively inexpensive and, most important, had suitable equilibrium relationships. The system was not chosen because of any commercial application.

Equilibrium distribution data for these acids, alone and in mixtures at room temperature, were determined. The agreement with the less complete data of Herz and Fischer (2) is good.

As an example of the extension of the results to a system in which separation is required in a commercial application, two runs were made on the five-component system, thorium nitrate - neodymium nitrate - ammonium thiocyanate - water - n-amyl alcohol. Equilibrium data for this system have been reported (1). In this case it was desired to separate the thorium from the neodymium, the latter being representative of the entire rare earth group. Ammonium thiocyanate served as a separating agent.

Method Of Calculation

Scheibel (5) proposed an essentially algebraic method for calculating the course of an extraction process which separates two solutes by the use of two immiscible solvents. In the present work, a graphical method is proposed which accomplishes the same result and possesses several advantages over the algebraic method. The stages are stepped off between equilibrium and operating lines. Reflux lines are also used and allowance is made for the effect of concentration on the equilibrium curves.

Results

Preliminary runs with pure succinic and pure oxalic acids at three different percentages of reflux established that each stage represented exactly one equilibrium contact. Runs with mixtures of the two acids were arranged in groups to show the effect of percentage reflux, solvent-to-water ratio, and feed concentration on the purity of oxalic acid in the aqueous

product and on the fraction of oxalic acid present in the feed which is recovered in a purified form. In all cases, purity and recovery varied in opposite directions. The use of reflux definitely improved the purity of product but decreased the recovery. Similarly, purity increased and recovery declined with increasing solvent-to-water ratio. The equilibrium relationships of the system are such that product purity decreases slightly with increasing feed concentration.

The results of the five-stage extraction system were also calculated from the equilibrium data using the step-wise graphical method. The small effect on the equilibrium distribution of one solute between the two solvents due to the presence of the other solute was taken into account. The agreement between experimental and calculated values was close in all cases.

The use of reflux in this system made it possible to improve the purity with a given number of stages at a fixed alcohol-to-water ratio. Alternatively, the use of reflux would have made it possible to obtain the same product purity with a reduced number of stages or with a smaller alcohol-to-water ratio. This would be of importance when a large number of stages is required for a given separation or when the solvent used is costly.

As already mentioned, these experimental results were obtained with only that portion of a complete extraction unit on one side of the feed. The requirements of a complete unit were calculated for fixed terminal concentrations. The recovery is set by these conditions and the beneficial effects of returning reflux were found to be smaller.

The experimental results from the two runs with the thorium - neodymium system are tabulated below. The aqueous feed was the same for both runs. It was 0.76 molar in ammonium thiocyanate and contained 4.21 and 4.73 grams/liter of thorium and neodymium, respectively.

EXTRACTION OF MIXTURES OF THORIUM AND NEODYMIUM

Purity of Product (Per cent Neodymium)		Per cent Recovery Neodymium	Per cent	Ratio Alcohol-
Experimental	Calculated	Experimental	Reflux	to-Water
74.3	81.5	87.5	0	2.16
92.5	—	58.7	75	2.07

The use of reflux increased the purity of the neodymium product from 74.3 to 92.5 per cent but caused a lower product recovery. In this case, where thiocyanate was used as a separating agent, the use of reflux had an added advantage in that the concentration of the agent was maintained at a higher level than would have been possible if pure alcohol had been introduced to the extractor instead of reflux. It is especially advantageous to return reflux when the separation per stage is higher or at least does not decrease with increasing concentration. This was particularly true of the thorium-neodymium system for which increasing the concentration of the separating agent, ammonium thiocyanate, improves the separation per stage.

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VITA

The author was born August 23, 1922 in Litchfield, Illinois. He received his elementary and secondary education in St. Patrick parochial school of Kankakee, Illinois. He attended the University of Illinois from 1939 to 1943, receiving a Bachelor of Science degree in chemical envineering. He was employed as research associate in the Chemical Warfare Service Development Laboratory at the Massachussetts Institute of Technology from 1943 to 1944, when he entered the naval service. He was honorably discharged from the navy in June, 1946, and entered the graduate school of the University of Illinois in the same month. He was employed as research assistant on contract with the Office of Naval Research during the academic year 1946-1947, investigating rare earth problems. He received the degree of Master of Science in chemical engineering in June, 1947. The time since that date has been spent pursuing studies leading to the doctorate. The author has also held for one semester each a teaching assistantship in physical chemistry and a University fellowship.

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